lead to considerable error if the dead-space is appreciable. For the case where the reaction results in a decrease of pressure, reactant will diffuse in from the dead-space, and the appropriate modifications of the above derivation give

$$R = N(1 + s) - N_0 s \qquad (6)$$

and

$$N_{\text{final}}/N_0 = s/(1 + s) \qquad (7)$$

where

$$s = aq/1 - q$$

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The Preparation of Perrhenic Acid

BY J. T. DOBBINS AND J. K. COLEHOUR

In connection with an investigation which was being carried out in this Laboratory, it became necessary to prepare some perrhenic acid. The usual method for preparing this acid consists of the decomposition of potassium perrhenate into potassium oxide, rhenium dioxide and rhenium by heating it in an atmosphere of hydrogen. The resulting residue is leached with water to dissolve the potassium oxide. Then the rhenium dioxide and rhenium are heated in an atmosphere of oxygen and are converted into perrhenic anhydride which is volatilized and absorbed in water to form the perrhenic acid.

As the sublimation of the anhydride gave considerable trouble, some modification of the method by which this difficulty might be avoided was sought. The fact that rhenium dioxide is oxidized by hydrogen peroxide suggested the following method. The residue of rhenium dioxide and rhenium, obtained as above, is placed in a combined flask and reflux condenser, a small quantity of water added and treated with 30% hydrogen peroxide. As the reaction is very vigorous at first, the hydrogen peroxide must be added in small portions. After the reaction slows down, the flask is heated gently until the solution becomes colorless and then refluxed vigorously for thirty minutes. Invariably, a small white precipitate appears in the solution, due possibly to occlusion of potassium oxide in the residue.

To prevent the volatilization of perrhenic acid, the solution is concentrated either in the air or over concentrated sulfuric acid. The evaporation is allowed to continue until the solution becomes a pale yellow viscous liquid.

To remove any potassium perrhenate the viscous liquid is taken up in 95% alcohol and filtered. The alcoholic solution is evaporated to remove the alcohol and diluted with water to the desired concentration.

The method is easily carried out and gives a better yield than the one now used.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride. VII. The Rearrangement of Isopropyl Salicylate and the Condensation of Propylene with Salicylic Acid

BY W. J. CROXALL, F. J. SOWA AND J. A. NIEUWLAND

The condensation of propylene with phenol in the presence of boron fluoride[1] has been found to yield alkyl substituted phenols and phenyl ethers. The purpose of this work was to investigate the influence of a carboxyl group in a phenolic compound on the course of condensation of propylene in the presence of boron fluoride, and for this purpose salicylic acid was used. The rearrangement of isopropyl salicylate was also investigated to show the course of the condensation of propylene with salicylic acid.

The rearrangement of isopropyl phenyl and cresyl ethers[2,3] and the allyl ethers of salicylic acid[4] have been studied. The use of boron fluoride as a catalyst for the condensation of olefins with fatty acids, aromatic acids, benzene and various substituted benzenes will soon be published.[5]

The action of propylene on salicylic acid in the presence of boron fluoride may be represented as taking place through a series of condensations and subsequent rearrangements. For example, pro-

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(1) Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 3694 (1932).

(2) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).

(3) Niederl and Natelson, *ibid.*, **53**, 1928 (1931).

(4) Claisen, *Ann.*, **418**, 69–120 (1919).

(5) Sowa and Nieuwland, unpublished work, University of Notre Dame, Notre Dame, Indiana.

pylene first condenses with salicylic acid to form isopropyl salicylate which then undergoes rearrangement with the entry of the isopropyl group into the ring, leaving a substituted acid which condenses with another molecule of propylene to form an ester which undergoes rearrangement as before, etc. The products isolated were: isopropyl salicylate; 2-hydroxy-3-isopropylbenzoic acid; isopropyl 2-hydroxy-3-isopropylbenzoate; 2-hydroxy-3,5-diisopropylbenzoic acid; isopropyl 2-hydroxy-3,5-diisopropylbenzoate and a trace of isopropyl 2-hydroxy-5-isopropylbenzoate. If the reaction is allowed to go to completion practically a theoretical yield of isopropyl 2-hydroxy-3,5-diisopropylbenzoate is obtained. The final condensation may be represented as

$$HOC_6H_3(C_3H_7)_2CO_2H + H_2C{=}CH{-}CH_3 \longrightarrow HOC_6H_3(C_3H_7)_2CO_2C_3H_7$$

Boron fluoride forms coördinate compounds with various acids and esters.[6] Salicylic acid absorbs boron fluoride and probably similarly forms a coördinate covalent compound with the hydroxyl oxygen of the carboxyl group, this coördination making condensation possible by causing the hydrogen on the carboxyl group to become more labile. The boron fluoride, after the condensation with propylene, forms a coördinate link with the ester and this weakens the bond between the oxygen and carbon of the ester group, causing rearrangement.

The structure of these compounds was proved by hydrolyzing the esters, identifying the acids, with the exception of 2-hydroxy-3,5-diisopropylbenzoic acid, and decomposing the acids into their corresponding phenols. The 2-hydroxy-3,5-diisopropylbenzoic acid is a new compound and was definitely proved by decomposing into the 2,4-diisopropylphenol.[1] The 2-hydroxy-3-isopropylbenzoic acid[7] as well as the 2-isopropylphenol is known.[1]

In the rearrangement of isopropyl salicylate the 2-hydroxy-3-isopropylbenzoic acid was not isolated, due to the presence of some salicylic acid, but was decomposed and the 2-isopropylphenol was definitely identified.

It is a very interesting fact that neither during the condensation of propylene with salicylic acid, nor during the rearrangement of isopropyl salicylate, were there any alkoxy derivatives formed. The products were all phenolic compounds. This is probably the result of a greater tendency for boron fluoride to coördinate with the carboxy or carbalkoxy than the phenolic group.

Experimental Part

Condensation of Propylene with Salicylic Acid.—Boron fluoride (4 g.) was added to 35 g. of salicylic acid suspended in 210 g. of heptane. Propylene was passed into this mixture for three days under a pressure of 8–10 cm. of mercury. During the course of the reaction a few grams more of boron fluoride had to be added. When approximately 1.25 moles of propylene was absorbed the reaction was stopped. The mixture was washed with a sodium carbonate solution, dried over potassium carbonate (anh.) and fractionated under reduced pressure after removing the heptane at atmospheric pressure. Fifteen grams of product boiling at 120–155° (18 mm.) and 36 g. boiling at 155–170° (18 mm.) were obtained.

From a number of condensations the products boiling 115–155° (18 mm.) were carefully fractionated and two definite fractions were obtained which boiled at 120–122° (18 mm.); sp. gr. 1.0101 (25°); n^{25}_D 1.5003; and 147–149° (18 mm.); sp. gr. 0.9988 (25°); n^{25}_D 1.5006.

The fraction of b. p. 120–122° (18 mm.) was identified as isopropyl salicylate by saponification and identification of the resulting isopropyl alcohol and salicylic acid.

Similarly the fraction of b. p. 147–149° (18 mm.) on saponification gave 12 g. of isopropyl alcohol from 41 g. of the compound, together with an acid (2-hydroxy-3-isopropylbenzoic acid[7] recrystallized from heptane m. p. 72°) which on heating to 200° gave 17 g. of 2-isopropylphenol.

The fraction of b. p. 155–170° (18 mm.) was refractionated several times to give a fraction, b. p. 163–165° (18 mm.); sp. gr. 1.0296 (25°); n^{25}_D 1.5124. This was proved to be isopropyl 2-hydroxy-3,5-diisopropylbenzoate in the same manner as above. Isopropyl alcohol and an acid of m. p. 115.2° were isolated. This acid was proved to be 6-hydroxy-3,5-diisopropylbenzoic acid by decomposing into the 2,4-diisopropylphenol, b. p. 248°; sp. gr. 0.9522 (25°); n^{25}_D 1.5124.

The Rearrangement of Isopropyl Salicylate.—Into 42 g. of isopropyl salicylate 12 g. of boron fluoride was absorbed and the contents refluxed for twenty minutes. After treatment with sodium carbonate and recovering the acids from this layer, the acids were very evidently a mixture as indicated by the melting range. The mixture was decomposed as before and 8 g. of 2-isopropylphenol and a trace of 4-isopropylphenol were isolated.

Further work is being done on the condensation of olefins with other hydroxybenzoic acids and the ethers and esters of hydroxyaromatic acids.

Summary

The condensation of propylene with salicylic acid in the presence of boron fluoride to give the alkyl substituted isopropyl esters has been accomplished.

Isopropyl salicylate has been rearranged to the 2-hydroxy-3-isopropylbenzoic acid.

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[6] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

[7] Filete, *Gazz. chim. ital.*, **16**, 126 (1886).

The course of the condensation has been shown to be a series of condensations and subsequent rearrangements.

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[Contribution from the Chemical Laboratory of Harvard University]

The Reactive Methyl Group in Toluene Derivatives. I. Oxidation with Selenium Dioxide and Cleavage of Benzylpyridinium Halides

By C. Harold Fisher

That certain toluenes possess an active methyl group,[1] comparable in some cases with the methyl group of acetophenone, has been long known. The results of a further study of the reactivity of the toluene methyl group are reported below under separate headings.

Oxidation with Selenium Dioxide.—It was found that conditions more drastic than those required for acetophenone[2] (refluxing in alcohol solution) are necessary for oxidation of toluene derivatives. Even 2,4-dinitrotoluene and 2,4,6-trinitrotoluene, which might be expected to give either nitrobenzaldehydes or nitrocresols,[3] were unattacked by selenium dioxide in boiling alcohol, and in boiling dioxane. However, it was found possible in several cases to cause oxidation at higher temperatures. At the refluxing temperature *p*-nitrotoluene was converted in poor yield into *p*-nitrobenzoic acid. Oxidation proceeded more satisfactorily and under less drastic conditions in the case of the benzyl halides. Nitrobenzaldehyde was obtained in good yield from *p*-nitrobenzyl bromide, and benzyl chloride was oxidized to benzaldehyde and a small amount of benzoic acid. Whether these benzyl halides were oxidized as such or underwent a preliminary hydrolysis to the corresponding benzyl alcohol[4] is not known. The oxidation of *p*-nitrobenzal bromide was more difficult than that of *p*-nitrobenzyl bromide; the product was *p*-nitrobenzoic acid. To ascertain the effect of additional phenyl and nitrophenyl groups the oxidation of diphenylmethane, 4,4′-dinitrodiphenylmethane and triphenylmethane was studied. It was found that none of these substances is oxidized by selenium dioxide in boiling alcohol, but that diphenylmethane and triphenylmethane are converted into benzophenone and triphenylcarbinol, respectively, at higher temperatures.

Cleavage of Benzylpyridinium Halides.—The halomethyl group of phenacyl halides[5] is quickly replaced by an hydroxyl group by condensation with pyridine and treatment with alkali of the pyridinium salt thus formed. The corresponding transformation (*p*-nitrobenzyl halide into *p*-nitrophenol) was not caused by the action of either alkali or alkaline hypobromite on the *p*-nitrobenzylpyridinium halides. No alkali-soluble products were formed with alkali treatment. However, alkaline hypobromite reacted almost at once with *p*-nitrobenzylpyridinium bromide, and with the corresponding chloride, to give good yields of *p*-nitrobenzoic acid. That this conversion of *p*-nitrobenzylpyridinium halides into *p*-nitrobenzoic acid proceeds through a brominated intermediate instead of by direct oxidation is suggested by the speed of the reaction, and the behavior of *p*-nitrobenzylpyridinium bromide toward bromine water: at once there was formed a yellow, flocculent precipitate which in turn reacted with alkaline hypobromite to give a good yield of *p*-nitrobenzoic acid. Apparently the nitro group is necessary for this transformation, since benzyl pyridinium chloride under the same conditions was found to yield resinous products, of which only a negligible portion was alkali-soluble.

Experimental

Selenium Dioxide Oxidations.—In the experiments described below equimolar quantities of the toluene derivative (0.05–0.1 mole) and selenium dioxide were dissolved in alcohol under an air-cooled return condenser, and the temperature of the mixture was brought to the desired value with an oil-bath or free flame, allowing some or all the alcohol to distil. Some products (benzoic acid and *p*-nitrobenzaldehyde) were isolated by extraction with hot water. Triphenylcarbinol was separated from selenium by filtering a hot alcohol solution; the liquid products were decanted and distilled. The phenylhydrazones of benzaldehyde and *p*-nitrobenzaldehyde melted, respectively, at 154–155.5° and 158.5–159.5°. Benzoic acid in

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(1) For references see Chardonnens, *Helv. Chim. Acta*, **16**, 1295 (1933).

(2) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).

(3) Hepp, *Ann.*, **215**, 344 (1882).

(4) Astin, Newman and Riley, *J. Chem. Soc.*, 391 (1933).

(5) Babcock and Fuson, This Journal, **55**, 2946 (1933); Kröhnke, *Ber.*, **66**, 1386 (1933).